## CLAIMS

1. Perfluorodiacylperoxides having the following structures:

wherein:

when  $R_f$  is F,  $R_f$ ,  $R_f$ , are both  $-CF_3$ .

when  $R_f$  is -CF3,  $R_f$ , and  $R_f$ , are C.-C3 linear or branched perfluorooxyalkyl groups;

wherein:

 $R_{\nu}$  is selected from F, perfluorooxyalkyl,  $C_1-C_3$  linear or branched perfluoroalkyl;

 $X_1, X_2$  are selected from F, perfluoroalkyl,  $C_1 - C_3$  linear or branched perfluorooxyalkyl.

$$CF_2$$
  $CX_3$   $- C(0) - O - O - C(0) - CX_3  $CF_2$   $CF_2$   $CF_2$   $CF_2$   $CF_2$   $CF_2$$ 

wherein:

$$n = 1-3$$

 $X_3$  is selected from F,  $C_1 - C_3$  linear or branched perfluoro-

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alkyl, with the proviso that for n=3,  $X_3$  cannot be F; said perfluorodiacylperoxides meet the following condition: the thermal decomposition constants  $K_d$  (sec<sup>-1</sup>) in the presence of water do not undergo substantial variations with respect to the thermal decomposition constants in absence of water.

- 2. A polymerization process of one or more fluorinated monomers wherein the perfluorodiacylperoxides according to claim 1 are used as polymerization initiators.
- 3. A polymerization process according to claim 2, wherein the polymerization is carried out in aqueous medium, in suspension, in emulsion or in microemulsion.
- 4. A polymerization process according to claims 2-3, wherein at temperatures of the order of 50°-80°C, the perfluoro-diacylperoxides of structure (C) or the compound of structure (A) having the formula:

are used.

5. A polymerization process according to claims 2-3, wherein at temperatures of the order of -20° - +25°C, the perfluorodiacylperoxides of structure (A) of formula:

are used, wherein when  $R_{\text{f}}$  is  $-CF_3$ ,  $R_{\text{f}}$ , and  $R_{\text{f}}$ , are  $C_1-C_3$  linear or branched perfluorooxyalkyl groups.

- 6. A polymerization process according to claims 2-5, wherein the fluorinated monomers are selected from:
  - $C_2$ - $C_8$  perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropene (HFP);
  - $C_2$ - $C_8$  hydrogenated fluoroolefins, such as vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene,  $CH_2$ =CH- $R_f$  perfluoroalkylethylene, wherein  $R_f$  is a  $C_1$ - $C_6$  perfluoroalkyl, hexafluoroisobutene;
  - $C_2$ - $C_8$  chloro-fluorolefins, such as chlorotrifluoroe-thylene (CTFE);
  - $CF_2$ =CFOR<sub>f</sub> (per)fluoroalkylvinylethers (PAVE), wherein  $R_f$  is a  $C_1$ - $C_6$  (per)fluoroalkyl, for example  $CF_3$ ,  $C_2F_5$ ,  $C_3F_7$ ;
  - $CF_2$ =CFOX (per) fluoro-oxyalkylvinylethers, wherein X is: a  $C_1$ - $C_{12}$  alkyl, or a  $C_1$ - $C_{12}$  oxyalkyl, or a  $C_1$ - $C_{12}$  (per) fluorooxyalkyl having one or more ether groups;
  - perfluorodioxoles, such as 2,2,4trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), 2,2bis-trifluoromethyl-4,5-difluoro-dioxole (PPD);

- sulphonic monomers, such as CF<sub>2</sub>=CFOCF<sub>2</sub>CF<sub>2</sub>SO<sub>2</sub>F;
- fluorinated dienes such as CF<sub>2</sub>=CFOCF<sub>2</sub>CF<sub>2</sub>CF=CF<sub>2</sub>,

  CF<sub>2</sub>=CFOCCl<sub>2</sub>CF<sub>2</sub>CF=CF<sub>2</sub>, CF<sub>2</sub>=CFOCF<sub>2</sub>OCF=CF<sub>2</sub>,

  CF<sub>2</sub>=CFOCF<sub>2</sub>OCCl=CF<sub>2</sub>, CF<sub>2</sub>=CFOC(CF<sub>3</sub>)<sub>2</sub>OCF=CF<sub>2</sub>.
- 7. A polymerization process according to claims 2-6, wherein the perfluorodiacylperoxide initiator is fed in a continuous way or by a single addition at the starting of the polymerization.
- 8. A polymerization process according to claims 2-7, wherein the amount of perfluorodiacylperoxide initiator is in the range 0.0001%-5% by moles with respect to the amount of the fed monomers.